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(54) **Chlorine-free composite rocket propellant.**

(57) A stable chlorine-free solid rocket propellant composition containing a low energy binder component having a heat of explosion value not exceeding about 350 cal/g which comprises a polyether or polyester-based polymer and at least one energetic plasticizer and further comprising, a nitrate salt and/or phase-stabilized nitrate salt as oxidizer component, a Mg/Al alloy of limited Mg content as a fuel component, and a burn rate catalyst.

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The present invention relates to a class of thermally stable modified double based rocket propellant compositions of a chlorine-free type that utilize inorganic nitrate-based salt(s) as an oxidizer component and a magnesium/ aluminum alloy as a fuel component.

There are two main types of solid rocket propellants in present use, the double base type and the composite type. Because of serious and long standing problems involving the brittleness of double based propellants under low temperature conditions and their detonation characteristics, composite type propellants are favored for use in large rockets and rocket boosters.

Composite-type propellants generally contain an inorganic oxidant and a fuel component incorporated into an elastomeric-type binder which is capable of being successfully cast and cured, in situ, while bonded to the inside of a rocket or booster casing. A high degree of reliability and precision in the geometry of the cast is necessary.

Double base type solid rocket propellants of the type used in the present invention comprise at a minimum two principal components, a nitrate ester type plasticizer in combination with a high molecular weight polymer such as nitrocellulose. Because of their high burn rate, thermal stability plus high loading potential with conventional binders and plasticizers, inorganic perchlorate salt(s) such as ammonium perchlorate have been widely used as major oxidant components in many composite formulations.

An example of a composite formulation containing inorganic perchlorate salts is found in U.S. Patent 3,350,245, Dickinson, which discloses the use of a crosslinked elastomeric binder with an oxidizer such as nitrates or perchlorates. The preferred oxidizers are ammonium perchlorate and lithium perchlorate. A plasticizer is used to modify the physical properties of the propellant. Minor constituents such as antioxidants, burning rate modifiers including organic boron compounds and pulverized metals were disclosed (including magnesium aluminum alloys having a content of 5 to 15 parts by weight of magnesium and 95 to 85 parts by weight of aluminum).

Use of such oxidizers as the inorganic perchlorate salts, however, presents a serious problem due to the fact that the corresponding rocket exhaust includes a very high percentage (21%-22%) of hydrogen chloride, which constitutes both a health hazard and a potential environmental pollutant. In U.S. Patent 4,158,583, the HCl exhaust is indicated to have a potential to disrupt the natural ultraviolet radiation shield in the stratosphere. Therefore, a high performance propellant without the HCl emissions is very desirable.

As a result, continuing attempts have been made (as in the Cahill et al U.S. Patent 3,445,304 and the Anderson U.S. Patent 4,158,583 discussed below) to wholly or partly substitute nitrate-based non-chlorine-containing salts in place of perchlorate salts as a primary oxidizer component.

In U.S. Patent 3,445,304, a solid rocket propellant comprising ammonium nitrate oxidizer, polymeric binders, burning rate modifiers such as boron, antimony or titanium dioxide and nitrocellulose was disclosed. The burning rate modifiers were chosen to provide a uniform burning rate of the rocket propellant.

In U.S. Patent 4,158,583, is described a high performance propellant having greatly reduced hydrogen chloride emission as a result of a reduced level of ammonium perchlorate oxidizer being present as compared to the prior art. A binder component comprising an elastomeric hydrocarbon, curing ingredients and plasticizer, an ammonium nitrate primary oxidizer a powdered metal fuel such as aluminum and a small amount of a secondary oxidizer such as ammonium perchlorate or a nitramine such as HMX (cyclotetramethylenetetranitramine) or mixtures thereof.

One recent attempt to prepare a halogen free solid rocket propellant was described in U.S. Patent No. 5,076,868, Doll et al., in which ammonium nitrate oxidizer was used with powdered magnesium fuel and an optional binder such as polyoxypropylene glycol. Doll et al. state that the use of magnesium powder without aluminum powder provides the desired combustion without slag formation and without the addition of high energy ingredients. A problem remains with the use of magnesium powder due to it being a safety hazard due to ignition sensitivity to electrostatic energy.

The above described attempts to reduce the use of HCl emitting solid rocket fuels have had limited success thus far, (a) because of high volumetric solids loading which results in difficulty in mixing and casting the combined formulation, (b) a low burn rate with low combustion efficiency, and (c) potential thermal instability due to a rapid depletion of conventional stabilizers under moderate heat in the presence of various burn rate catalysts and metal fuel components.

The present invention provides a solid propellant which does not evolve substantial amounts of hydrogen chloride in the firing exhaust and provides a stable, chlorine-free high-energy modified double based propellant composition of suitable burn rate and efficiency.

The present invention provides a stable solid rocket propellant composition comprising, in combination:

(A) a low energy binder component having a total heat of explosion (HEX) not exceeding about 350 cal/gram, where said binder component comprises a polyether- or polyester-, based polymer or

copolymer(s) or combinations thereof; at least one energetic plasticizer component comprising at least one member selected from the group consisting of a nitrato alkyl nitramine, triethylene glycol dinitrate (TEGDN), 1,2,4- butanetriol trinitrate (BTTN), diethylene glycol dinitrate (DEGDN), trimethylolethane trinitrate (TMETN), nitroglycerin and mixtures thereof and at least one cure catalyst;

(B) an active amount of at least one nitrate-based oxidizer component comprising ammonium nitrate (AN) and/or phase-stabilized AN (a mixture of ammonium nitrate and a phase stabilizer such as metal oxides such as ZnO, NiO, KNO_3 or long chain aliphatic amines);

(C) an active amount of a fuel component comprising an Al/Mg alloy, wherein Mg does not exceed about 50% by weight of said alloy; and

(D) an effective amount of at least one propellant burn rate catalyst selected from the group consisting of amorphous boron, an amorphous boron/KNO_3 mixture, chromic oxide, ammonium dichromate, zirconium hydride, ultrafine aluminum oxide and cyclotetramethylene tetranitramine.

Suitable polyether- or polyester-, based polymer or copolymers for use in the binders include polytetramethylene adipate, polydiethyleneglycol adipate, polyethylene glycol, polytetrahydrofuran and copolymers thereof, polypropylene glycol, and a random copolymer of ethylene oxide and tetrahydrofuran. These polymers comprise about 3 to 15 percent by weight of the propellant composition.

The term "low energy binder component" is further defined as a total binder mixture having a (HEX) value within the range of about -750 cal/g to about +350 cal/g. Within the term "low energy" is a higher energy zone (i.e. about -195 cal/g up to about +350 cal/g) and a lower HEX energy zone (i.e. about -750 cal/g up to about -195 cal/g). The higher energy zone is most easily obtainable in a binder containing an effective amount of one or more high energy plasticizer components such as triethylene glycol dinitrate (TEGDN), 1,2,4- butanetriol trinitrate (BTTN), diethylene glycol dinitrate (DEGDN), trimethylolethane trinitrate (TMETN), and nitroglycerine (NG). Binders coming within the aforementioned lower HEX energy zone are most readily obtainable by utilizing a less energetic plasticizer component such as a nitrato alkyl nitramine, inclusive of methyl- ethyl-, propyl-, and butyl-nitrato ethyl nitramines and combinations thereof with more energetic materials. The total heat of explosion is determined by burning a small, but known, amount of propellant in a calorimeter bomb, which is purged of air, pressurized with nitrogen and exploded by use of an initiating means followed by cooling (non-adiabatically) to ambient temperature.

The energetic plasticizer components of the binder that are listed above are is used in a concentration of about 6 to 20% by weight of the propellant, the precise amount used, however, depends upon the choice of oxidizer component, the choice of polyether- or polyester-based polymer, the ratio of oxidizer-to-fuel (hereinafter O/F), the choice and amount of burn rate catalyst used to augment the propellant burn rate, and ultimately, the desired HEX value of the binder and propellant.

Previous to the present invention, use of such nitrate-based oxidizer components in place of perchlorate salts has been less than successful due to inherent low loading limitations, low energy content, and low burn rates (i.e. substantially less than about 0.2"/second) for the resulting propellant formulations.

The term "phase stabilized AN" denotes the nitrate salt premixed with a metal oxide such as zinc oxide, or nickel oxide or with a long chain aliphatic amine.

The term "active amount of nitrate-based phase-stabilized oxidizer component," assumes about 70-85% solids and a ratio of oxidizer component-to-fuel component within a range of about 1-2.5 parts to 1 part by weight. The nitrate-based phase-stabilized oxidizer component is preferably about 50 to 70 percent weight of the propellant composition.

The term "an active amount of a fuel component comprising a magnesium/aluminum (Mg/Al) alloy" denotes an amount which is compatible with the above-described oxidizer component and also is capable of increasing combustion efficiency and stability (compared with Mg alone).

For example, it has been found that a Mg/Al alloy, in which the amount of elemental Mg does not substantially exceed about 50% by weight of the alloy (preferably about 20% - 50%) and the amount of alloy component in the propellant formulation varies from about 15%-30%, or slightly higher, based on propellant weight, is compatible with an acceptable stabilizer depletion rate (see Table 1). In prior art compositions containing a magnesium metal fuel component it has been found that the magnesium had the undesirable effect of depleting nitrate ester stabilizers such as N-methyl-p-nitroaniline used herein in small amounts. Employing an alloy of magnesium and aluminum in the above prescribed ratios is an important feature of the present invention that greatly reduces the stabilizer depletion tendency of the magnesium. In general, a stabilizer depletion rate sufficiently low to assure a stable propellant life of 30 days at 158°F and 30 years at 77°F is considered marginally acceptable.

While an increase in the ratio of oxidizer component-to-metal fuel (O/F) within a propellant of the present invention does not appear to be directly correlated to increased burn rate, it is found to affect combustion efficiency and pollution potential, as well as overall booster reserve capacity. For present

purposes, a ratio of about 1-2.5 to 1, preferably 1.0-1.9/1 and most preferably 1.2-1.9/1 (O/F) is found generally acceptable for binders falling within a HEX (energy) range of about -750 cal/g to about +350 cal/g or possibly slightly higher.

The term "an effective amount of a propellant burn rate catalyst" denotes an amount sufficient to assure a burn rate exceeding .20" (where the burn rate is determined by burning strands of propellant in a pressurized calorimeter bomb) and an optimal value of about 0.30"/second or higher. It is normally necessary to include at least some burn rate catalyst within the propellant that is compatible with the nitrate ester plasticizer. In the present instance "an effective amount of a propellant burn rate catalyst" constitutes a range of up to about 20% by weight of the propellant and preferably about 1-16% by weight of the propellant is amorphous boron, amorphous boron/potassium nitrate or mixtures thereof to best assure a burn rate suitable for military or space purposes. Other burn rate catalysts that can be used in amounts up to 10% by weight of the propellant are selected from the group consisting of chromic oxide, ammonium dichromate, zirconium hydride, ultrafine aluminum oxide and cyclotetramethylene tetranitramine. Mixtures of these burn rate catalysts can also be used.

Propellant compositions within the scope of the present invention also preferably include relatively small amounts of art-recognized additives including isocyanate and polyisocyanate curative agents for the binder such as Desmodur® N-100 (a trifunctional isocyanate with about 3.7 functionality); cure catalysts such as maleic anhydride, triphenyl bismuth and mixtures thereof for the crosslinking of the polyether and polyester-based polymers of the binder; and stabilizers such as nitroaniline or alkyl derivatives thereof, to prevent decomposition of the nitrate esters. Preferably a mixture of diisocyanate and polyisocyanate curatives are used to produce a solid rocket motor fuel of the desired hardness. The total amount of such additives, however, generally does not exceed about 2% by propellant weight.

Other features, advantages and specific embodiments of this invention will become readily apparent to those exercising ordinary skill in the art after reading the foregoing disclosures. In this regard, while specific embodiments of this invention have been described in considerable detail, variations and modifications of these embodiments can be effected without departing from the spirit and scope of the invention as disclosed and claimed.

The present invention is further illustrated but is not limited by the following examples and tables:

Example I

Test batches of chlorine-free phase-stabilized nitrate-based propellant were prepared for conventional microwindow bomb and subscale motor testing procedures to ascertain the effect of (a) various Mg/Al alloys as fuel components, (b) variations in oxidizer/fuel ratios, and (c) effect of burn rate catalyst on ammonium nitrate-based propellent burn rates.

A. Test propellants of different energy content utilizing different Mg/Al alloy ratios as fuel components were prepared in one pint and one gallon amounts by mixing 12 parts by weight of low molecular rate polyglycol adipate prepolymer with 10.3 parts triethylene glycol dinitrate energetic plasticizer (the amount being based on estimated HEX values of -750 cal/g and -195 cal/g), 0.04 parts N-methyl-p-nitroaniline, 0.06 parts of DER® 331 (Dow Chemical Company epoxy bonding agent) for about 20 minutes at 49°C. To this mixture was then added ammonium nitrate (39.3 parts); after 15 minutes of mixing, 0.04 parts triethylene tetranitramine bonding agent were also added, and the mass agitated at 49°C under vacuum for 30 minutes. To this mass was added 23.7 parts of magnesium/aluminum alloy (-325 mesh) of desired Mg content or ratio as fuel component, plus a fine mix of ammonium nitrate (13.1 parts). After 30 minutes of additional mixing under partial vacuum at 49°C, the mixer was vented and isocyanate curative agents and a curing catalyst were added as a premix comprising

Isophorone diisocyanate (.79 parts)
N 100 polyfunctional isocyanate (.46 part)
Triphenyl bismuth catalyst (.05 part)
Maleic anhydride (.10 part);

and the entire mixture was then mixed under vacuum for an additional 30 minutes. The mass was cast into paper molds to obtain 600 gram and 6,000 gram test samples and cured for five (5) days at 49°F. The samples were identified as TA-1 through TA-10 as shown in Table 1 where results with respect to the effect of Mg content in the fuel, energy content, burn rate and stability are reported. Exotherms and significant stabilizer depletion rates are noted at 70°C for alloys exceeding about 50% Mg and HEX values of -195 or higher. The depletion rate was measured by liquid chromatographic technique utilizing a Varian/model 401/402 Data Station with silica gel column.

Table 1

Sample #	% Mg in Fuel Alloy	HEX Value of Binder cal/g	Burn Rate in/sec	Exotherms temp °C	70°C MNA% Depletion Rate/Day
TA-1	20	-580	.125	NONE	---
TA-2	20	-195	.150	NONE	0.01
TA-3	40	-580	.162	NONE	---
TA-4	40	-195	.175	NONE	0.02
TA-5	50	-580	.187	---	---
TA-6	50	-195	.187	147	0.04
TA-7	60	-580	.225	---	---
TA-8	60	-195	.200	124	0.05
TA-9	80	-580	.275	---	---
TA-10	80	-195	.230	166	0.11

B. The test propellant of Example IA was modified by utilizing only 23.7 parts of 40% Mg in the Mg/Al alloy fuel component and a -195 cal/g binder HEX value but the weight ratio of phase-stabilized ammonium nitrate oxidizer-to-alloy (fuel) was varied from 1.2-1.9 to 1. The resulting burn rates of the resulting propellants TB-11, TB-12, TB-13, and TB-14 are recorded in Table 2 below:

TABLE 2

Sample #	Oxidizer/Fuel	Burn Rate (inches/sec)
TB-11	1.25/1	0.170
TB-12	1.50/1	0.190
TB-13	1.80/1	0.190
TB-14	1.90/1	0.170

C. Test propellants were prepared in the manner of Example 1A, but utilizing a 45/55 Mg/Al alloy, a HEX value of about -195 cal/g and varying amounts (ie. 2%, 6%, 8%, 10%, 12% and 16% by weight) of amorphous boron as burn rate catalyst with and without supplemental KNO_3/AN. The resulting propellant samples, identified respectively as TC-1, TC-2, TC-3, TC-4, TC-5, TC-6, TC-7, TC-8 and TC-9 were tested for burn rate in a micro bomb and the results reported in Table 3 below:

TABLE 3

Sample #	% Amorphous Boron	Burn Rate (LPs) (Inches/Sec.)
TC-1	2	0.205 0.201
TC-2	4	0.235 0.230
TC-3	6	0.265 0.262
TC-4	8	0.300 0.295
TC-5	10	0.325 0.325
TC-6	12	0.352 0.350
TC-7	16	0.412 0.415
TC-8	5 (With AN)	0.230 ---
TC-9	5 (with KNO_3/Stab. AN)	0.400 ---
Control	0	0.175 ---

Example II

Propellant samples (HEX-195/g) obtained in accordance with Example IA and identified as TA-2, TA-4, TA-6, TA-8 and TA-10 were stored for a 24 hour period at 70°C and 25% relative humidity. The samples were thereafter analyzed to determine the effect of Mg level on MNA (N-methyl p-nitroaniline) stabilizer depletion rate. Test results are reported in Table 1 (last column).

Claims

1. A stable solid rocket propellant composition comprising, in combination
   A. about 15 to 30 percent by weight of a low energy binder component having a total heat of explosion between about -750 cal/g and 350 cal/g, said binder component comprising
      (1) at least one polyether- or polyester- based polymer or copolymer(s) comprising about 3 to 15 percent by weight of said propellant composition;
      (2) at least one energetic plasticizer component comprising about 6 to 15 percent of said propellant composition; and
      (3) at least one cure catalyst;
   B. about 50 to 70 percent by weight of said propellant composition of at least one nitrate-based oxidizer component comprising ammonium nitrate and/or phase-stabilized ammonium nitrate;
   C. about 15 to 30 percent by weight of said propellant composition of an active amount of a fuel component comprising an Al/Mg alloy, wherein Mg content is a maximum of about 50% by weight of said alloy and wherein the ratio of oxidizer component to fuel component is within a range of about 1-2.5 to 1; and
   D. up to about 20 percent by weight of an effective amount of at least one propellant burn rate catalyst.

2. The propellant composition of claim 1 wherein in said binder said polyether- or polyester based polymer is selected from the group consisting of polytetramethylene adipate, polydiethyleneglycol adipate, polyethylene glycol polytetrahydrofuran and copolymers thereof, polypropylene glycol, and a random copolymer of ethylene oxide and tetrahydrofuran and said plasticizer component comprises at least one member selected from the group consisting of a nitrato alkyl nitramine, triethylene glycol dinitrate, 1,2,4- butanetriol trinitrate, diethylene glycol dinitrate, trimethylolethane trinitrate, nitroglycerin and mixtures thereof.

3. The propellant composition of claim 1 wherein the fuel component comprises about 20%-50% magnesium by weight of said alloy.

4. The propellant composition of claim 1 wherein about 1%-16% by weight of said propellant is said burn rate catalyst that is selected from the group consisting of amorphous boron, amorphous boron/potassium nitrate, and mixtures thereof and about 0-10% by weight of said propellant is said burn rate catalyst component that is selected from the group consisting of chromic oxide, ammonium dichromate, zirconium hydride, ultrafine aluminum oxide and cyclotetramethylene tetranitramine and mixtures thereof.

5. A method for increasing burn rate and efficiency while maintaining thermal stability of a solid propellant composition that emits a chlorine-free exhaust when burned comprising formulating a binder mass comprising a polyether-, or polyester-, based polymer and at least one energetic plasticizer component, with at least one cure catalyst, combining with said binder mass an oxidizer component comprising at least one inorganic nitrate salt, a fuel component containing aluminum and magnesium, and at least one burn rate catalyst wherein the choice and amount of energetic plasticizer and fuel component admixed therein is commensurate with a binder heat of explosion value not exceeding about 350 cal/g, wherein the oxidizer component is ammonium nitrate (AN), phase stabilized AN or mixtures thereof; wherein the fuel component is a Mg/Al alloy containing about 20 to 50 wt. % Mg; wherein the ratio of oxidizer component to fuel component is within a range of about 1-2.5 to 1.

6. The method of claim 5 wherein the binder heat of explosion value is within a range of about -195 cal/g to about 350 cal/g.

7. The method of claim 5 wherein the binder heat of explosion value is within a range of about -750 cal/g to about -195 cal/g.

8. The method of claim 5 wherein the ratio of oxidizer component-to-fuel component is within a range of 1.2-1.9 to 1.

9. The method of claim 5 wherein said polyether- or polyester based polymer is selected from the group consisting of polytetramethylene adipate, polydiethyleneglycol adipate, polyethylene glycol, polytetrahydrofuran and copolymers thereof, polypropylene glycol, and a random copolymer of ethylene oxide and tetrahydrofuran.

10. The method of claim 5 wherein the plasticizer component comprises a member selected from the group consisting of a nitrato alkyl nitramine, triethylene glycol dinitrate, 1,2,4- butanetriol trinitrate, diethylene glycol dinitrate, trimethylolethane trinitrate, nitroglycerin and mixtures thereof.

11. The method of claim 5 wherein when said burn rate catalyst is selected from the group consisting of amorphous boron, amorphous boron/KNO_3 or mixtures thereof said burn rate catalyst is about 0-20% by weight of said propellant and when said burn rate catalyst is chromic oxide, ammonium dichromate, zirconium hydride, ultrafine aluminum oxide and cyclotetramethylene tetranitramine and mixtures thereof said burn rate catalyst is about 0-10% by weight of said propellant.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 12 1582

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D,A	US-A-3 350 245 (L.A. DICKINSON) * column 1, line 22 - line 56 * * column 2, line 15 - column 3, line 17 * * column 3, line 66 - line 69 * * column 4, line 42 - column 5, line 11 * ---	1,5	C06B33/04 C06B45/10
A	US-A-3 044 911 (T.L. FRITZLEN) * column 3, line 12 - line 35 * * column 4, line 4 - line 63 * ---	1,5	
A	US-A-5 074 938 (MINN-SHONG CHI) * column 4, line 53 - column 6, line 33; claims * ---	1-11	
A	US-A-4 111 728 (J. RAMNARACE) * column 1, line 44 - line 68; claims * * column 2, line 41 - line 56 * * column 3, line 41 - line 52 * * column 4, line 6 - line 45 * ---	1,5	
A	US-A-5 067 996 (N.H. LUNDSTROM ET AL.) * column 3, line 59 - column 4, line 6 * ---	1,5	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
D,A	US-A-4 158 583 (R.A. FROSCH ET AL.) * column 1, line 19 - column 2, line 24; claims * ---	1,5	C06B
A	US-A-4 764 586 (G.E. MANSER ET AL.) * column 1, line 13 - column 2, line 2 * * column 5, line 38 - column 7, line 5 * * column 9, line 48 - column 10, line 19 * ---	1,5	
D,P,A	US-A-5 076 868 (D.W. DOLL ET ALL.) * column 1, line 5 - line 26; claims * -----	1-11	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	03 MAY 1993	SCHUT R.J.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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L : document cited for other reasons

& : member of the same patent family, corresponding document